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Dissociation of Shock-Compressed Liquid Hydrogen and Deuterium

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Abstract

Compression in a shock wave is followed by a large number of nonequilibrium processes, such as excitement of internal degrees of freedom, chemical reactions, and establishment of chemical equilibrium. Thermodynamic parameters of shock-compressed liquid hydrogen and deuterium are calculated on the basis of the developed model of the equation of a state (EOS) of two-component fluid mixtures with use of potential of intermolecular interaction of Exp-6. Comparison of the calculated parameters of a quasiequilibrium condition of the two-component mixtures which are formed as a result of dissociation at strong compression in a shock wave with experimental data allows concluding that the offered theoretical model EOS reliably describes thermodynamic properties of two-component fluid mixtures in the wide range of pressure and temperatures at chemical equilibrium.

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Keywords: perturbation theory; shock Hugoniot, intermolecular interaction potential Exp-6; nonequilibrium process; dissociation; chemical equilibrium

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Nomenclature

φ	intermolecular potential	P	pressure
ε	potential well depth	T	temperature
r_m	potential parameter	V	volume
α	potential parameter	R	gas constant
r	intermolecular distance	ρ	density of gas

1. Introduction

Properties of the compressed and warmed hydrogen are interest in connection with its considerable presence in the nature, and also in the atmosphere of giant planets.

Realness of the calculated thermodynamic parameters depends first of all on the accuracy of the applied equations of a state. Therefore the problem of receiving EOS which are reliably describing properties of multicomponent fluid mixtures with high pressures and temperatures is extremely important [1–3].

For thermodynamic calculations at high pressures and temperatures only physically reasonable models of the equations of state of dense fluids have to be used and no more widespread semi-empirical EOS which extrapolation in the interesting area of pressure and temperatures where there are no experimental data for calibration of such equations, can lead to obtaining absolutely incorrect data.

Rather large number of theoretical models of fluid systems is so far developed, and works on their improvement are continued [4–6]. The best modern perturbation theories and the integrated equations allow calculating thermodynamic properties of dense pure fluids with various types of intermolecular potentials with excellent agreement with results of modeling by Monte-Carlo and Molecular Dynamics.

However the offered techniques [4, 6] can be used only for those potentials of interaction (Lennard-Jones, Kikhara) for which they were developed

Therefore in this work theoretically reasonable EOS [7] of dense fluids constructed on the basis of the thermodynamic perturbation theory [8] and potentials of intermolecular interactions of Exp-6 which realness in the area of pressure and temperatures interesting us can be considered proved were applied to thermodynamic modeling of conditions of substance.

2. The theoretical model of equation-of-state

The perturbation theory KLRR [8] allows receiving EOS of fluids both at high pressures and temperatures, and at lower temperatures and density. This theory reproduces results of calculations of Monte-Carlo with a good accuracy for different types of interaction potentials, including Exp-6 potentials which realness is confirmed by many researches.

For the description of interaction of molecules of fluid mixture spherically symmetric Exp-6 potential (modified Buckingham potential) is used:

$$\varphi_{ij}(r) = \frac{\varepsilon_{ij}}{\alpha_{ij} - 6}\left(6\exp\left[\alpha_{ij}\left(1 - \frac{r}{r_{m,ij}}\right)\right] - \alpha_{ij}\left(\frac{r_{m,ij}}{r}\right)^6\right), r \geq c_{ij} \tag{1}$$

$$\varphi_{ij}(r) = +\infty, r < c_{ij} \tag{2}$$

where $\varepsilon_{ij} > 0$ and corresponds to the potential well depth ($\min[\varphi_{ij}(r)] = -\varepsilon_{ij}$), $r_{m,ij}$ is the distance between the centres of molecules at which the potential energy takes the minimum value ($\varphi_{ij}(r_{m,ij}) = -\varepsilon_{ij}$), and α_{ij} is the parameter determining the repulsive stiffness.

Potential Exp-6 is defined by three parameters, which values are defined in [2] and for the substances investigated in this work are presented in table 1. The unlike-pair Exp-6 parameters are additive, i.e. they follow the Lorentz–Berthelot combination rules [9].

Table 1. Parameters of the Exp-6 potential for the investigated substances.

Molecule	α	ε/*k*, K	r_m, A
H_2	10.6	36.9	3.67
H	10.0	110.0	1.55
D_2	11.2	30.4	3.49
D	11.0	50.0	2.1

To calculate the thermodynamic properties of a fluid system at a given temperature *T* and volume *V*, it is sufficient to know the Helmholtz energy of this system. The values of all the required thermodynamic parameters can be found by calculating the corresponding Helmholtz energy derivatives. The method, which allows us to calculate with a high level of accuracy the excessive Helmholtz energy of a two-component system consisting of two kinds of molecules that interact with each other through a spherically symmetric intermolecular pair potential, was described in detail in [7]. The reliability and efficiency of the theoretical EOS model of a two-component fluid (2f-model) proposed in [7] is proved by the good agreement between the MC simulation results over a wide range of a fluid's thermodynamic states [7].

3. Calculation results of thermodynamic properties of shock Hugoniots for H_2, D_2

Using offered in [7] the EOS model of a two-component fluid, calculation of shock Hugoniots for liquid hydrogen and a deuterium were carried out. Results are presented graphically to *PV*-and *TP*-coordinates in fig. 1, 2 in the wide range of pressure and temperatures (to 50 GPA and to 10000 K). Symbols in drawings showed experimental data and results of modeling of Monte-Carlo [10-15].

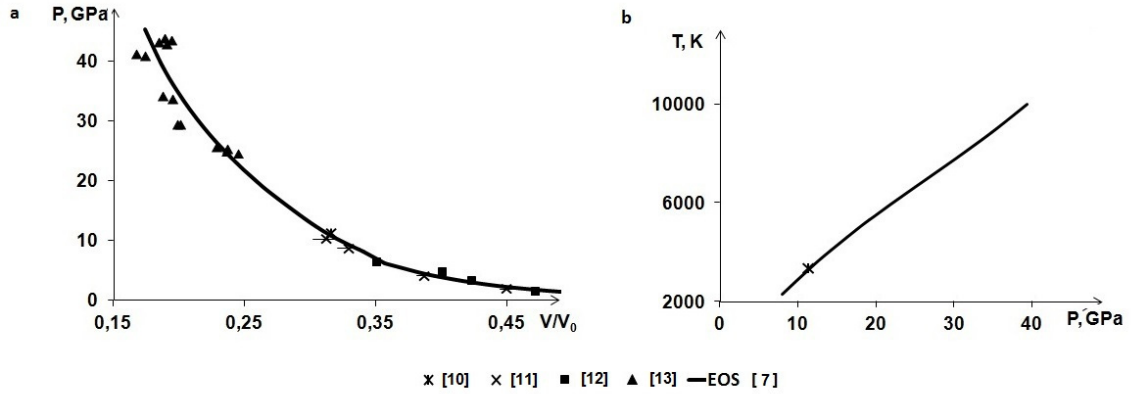

Fig. 1. Shock Hugoniot for liquid hydrogen in *PV*- (a) and *TP* (b) - coordinates. The initial state of the H_2 is characterized by the following parameters: T_0 = 23.5 K, ρ_0 =0.071 g/cm3, U_0=-2.016 kcal/mol.

From fig. 1, 2 it is visible that for the two-component mixtures which are formed at dissociation of molecules of hydrogen and deuterium the good consent of calculations on the basis of 2f-model with experimental data is observed.

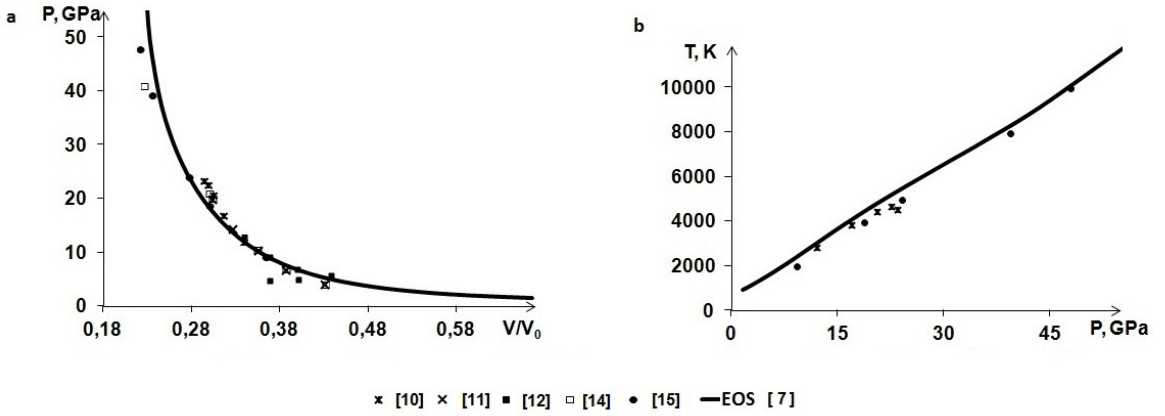

Fig. 2. Shock Hugoniot for liquid deuterium in *PV*- (a) and *TP* (b) - coordinates. The initial state of the D_2 is characterized by the following parameters: T_0 = 23.5 K, ρ_0 =0.171 g/cm3, U_0=2.126 kcal/mol.

4. Conclusion

On the basis of the KLRR version of perturbation theory the theoretical EOS model of a two-component fluid [7] with potentials of intermolecular interaction of Exp-6 is developed. With use this model calculations of thermodynamic parameters of shock and wave compression of liquid H_2 hydrogen and a deuterium of D_2 are calculated.

Comparison with experimental data and results of modeling of Monte-Carlo allows concluding that offered in [7] theoretical EOS model reliably describes thermodynamic properties of two-component fluid mixes in the wide range of pressure and temperatures.

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